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Research and Development Report

Minimum Release of Tributlytin to Prevent Macrofouling

by

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The minimum release of tri-and dibutyltin has been determined for both barnacles and hydrozoans. The test method involved perfusing a known flux of biocide through a polycarbonate membrane filter with the downstream surface of the membrane exposed to a natural population of fouling organisms. Results show that the minimum release of tributyltin to reduce attachment of 90% was 0.22 $\mu g/cm^2/day$, while 0.83 $\mu g/cm^2/day$ prevented hydrozoans from attaching. No minimum release rate could be calculated for the dibutyltin because the flux rates were not high enough to achieve a zero fouling condition.

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ABSTRACT

The minimum release of tri- and dibutyltin has been determined for both barnacles and hydrozoans. The test method involved perfusing a known flux of biocide through a polycarbonate membrane filter with the down stream surface of the membrane exposed to a natural population of fouling organisms. Results show that the minimum release of tributyltin to reduce attachment by 90% was 0.22 $\mu g/cm^2/day$, while 0.83 $\mu g/cm^2/day$ prevented hydrozoans from attaching. No minimum release rate could be calculated for the dibutyltin because the flux rates were not high enough to achieve a zero fouling condition.

Administrative Information

This task was performed as part of the Energy Block, under the direction of Mr. Bill Stoffel. The work was supervised by Mrs. J. Montemarano, David Taylor Research Center (DTRC), code 2841, under the Minimum Effective Release Rate task.

BACKGROUND

Improvements in hull design have permitted Navy ships to minimize hydrodynamic drag and thereby achieve maximum speed and range. Retaining these benefits depends on maintaining a clean, smooth hull, which is currently achieved by antifouling paints. The most effective antifouling paints are designed to release a biocide that prevents the attachment of, or quickly kills, settling organisms. However, modern AF coatings have release rates higher than necessary to prevent fouling. Excessive release of biocide threatens non-target organisms. This is of particular concern when many ships are berthed near areas

which contain economically or environmentally significant organisms. Minimizing the threat to non-target organisms requires limiting biocide release rates to the lowest level which is sufficient to prevent attachment.

Recently, environmental models have been developed to help predict negative impacts of excess biocide release. The models take into account such factors as tidal cycles, seawater chemistry, biocide toxicity, and rate of biocide degradation. Release rate predictions are based on laboratory and/or field measurements. However, depending on the technique used and the conditions under which the measurement is made (ie. pH, salinity, temperature, and hydrodynamic regime), reported rates for any given paint may vary by as much as an order of magnitude. It is unclear, therefore, how to predict exactly how much biocide is being released into the environment by an AF paint on a ship in service or a panel during exposure in the sea.

The recent increases in environmental concern have motivated development of antifouling coatings with minimum environmental impact to non-target organisms. In order to achieve this result, knowledge of the response of fouling organisms to toxin released from the surface into the seawater is required. Because tailoring of a new formulation to achieve a desired set of properties is a time-consuming and expensive process, it would be helpful for the paint maker to have knowledge of required effective release rates for particular antifouling agents prior to paint formulation. If this knowledge is not available, considerable efforts will have to be expended to fabricate a set of formulations which will have a wide enough range of

release rates to establish the relation between fouling and toxin release rate. These formulations would then have to be tested for both AF performance in marine exposure and release rate. The availability of a simple method to determine the relationship between AF agent release rate vs fouling response, and thus the minimum effective release rate for the Af agent, would greatly facilitate the development of AF paints without the need to formulate a large number of paints. Such a method is described here.

MATERIALS AND METHODS

The test system used was designed to pump a known volume of a tributyltin (TBT) solution of known concentration through a porous polycarbonate membrane which simulated a painted surface releasing biocides. Flux was varied to simulate a range of release rates. The test cell assembly was the same as used by Gates et al. (1) but constant flow rate was produced by a peristaltic multichannel pump rather than gravity flow from burettes. The polycarbonate membrane filters were exposed to seawater for 72 hours while known concentrations of tributyltin were perfused through each membrane. The seawater exposure site, Chesapeake Biological Laboratory in Solomons, Maryland, was chosen because barnacles, bryozoans, and hydroid larvae were active. After the 72 hour exposure the numbers of attached organisms were counted on the filter surfaces. Two controls for these experiments were used, one with the same flow as the experimental test cells but without tributyltin, and two test cells with no flow.

Test cells were Nuclepore 47mm Swin-lok™ aerosol filter holders which held the test surface, a 47mm polycarbonate membrane filter. The edge of the membrane was sealed with an silicone o-ring exposing only the central portion of the membrane to the seawater. The diameter of the exposed portion of the membrane was 41mm diameter or 128 mm^2.

The biocide delivery system was an Ismatec™ multichannel peristaltic cartridge pump capable of pumping at the desired low flow rate of 1 ml per hour. The flexible tubing used at the pump head was silicone Masterflex pump head tubing, the remainder of the system's tubing consisted of FEP teflon™ tubing chosen for its low TBT adsorption characteristics (2). The TBT adsorption characteristics of the flexible silicone tubing was evaluated prior to its use in these experiments. Various concentrations of tributyltin chloride (TBTCl) were allowed to contact the interior walls of the tubing for a 48 hr period. The TBT concentrations of these solutions were then measured and compared to the TBT concentrations of the original stock solutions. The difference between the two represents the amount of TBT that adsorbed onto the tubing walls. TBT concentrations were measured using a spectrofluorimeter (3) prepared by dilutions using artificial sea water.

Test solutions of TBTCl were mixed from a stock solution of 0.0161 grams tributyltin chloride in 250 ml methanol. Dilutions were then made from this solution to achieve a known flux (Table 1). Since the test solutions contained a small amount of methanol the control solutions also contained equal amounts of methanol without the TBT.

Table 1. Experimental flux rates using tri- and dibutyltin chloride.

Flux rate TBTCl $\mu g/cm^2/day$	Flux rate DBTCl $\mu g/cm^2/day$
1.22	2.13
0.84	1.02
0.66	0.84
0.41	0.66
0.22	0.41
0.05	0.22

The number of attached fouling organisms were determined by counting after a 72 hour exposure period. Only those organisms that actually settled on the membrane surface were counted. Membranes were then changed and the experiments repeated. A second set of identical experiments were conducted using dibutyltin chloride instead of the tributyltin (Table 1). The concentrations of the dibutyltin perfusing through the membranes were increased due to the suspected reduced toxicity of dibutyltin (4).

Statistical analysis was performed according to Draper and Smith (5) using a third order polynomial fit to the data in the region of the minimum effective release rate.

RESULTS

The results of these experiments have allowed a determination of the minimum release of tributyltin for effective control of both

barnacles and hydrozoans in the local estuaries at the 10% fouling level. The minimum tributyltin release curve for barnacles is shown in Fig. 1, and hydrozoans in Fig. 2. At the 95% confidence level 0.22 $\mu g/cm^2/day$ is required to prevent 90% of the available barnacles from attaching to the surface (Fig. 1). Hydrozoans required 0.83 $\mu g/cm^2/day$ to achieve the same 90% fouling free condition (Fig. 2).

The results for the dibutyltin release rates are not as clear. It was not possible to determine the minimum release rates of the dibutyltin for these organisms since the experimental flux values were not high enough to achieve the 90% fouling free level (Figs. 3 and 4). More experimentation at higher flux values will be necessary before the minimum effective release rates can be determined for the dibutyltin.

The raw data for these experiments can be found in Appendix A.

DISCUSSION AND CONCLUSIONS

This data represents the first attempt to quantitatively determine the minimum effective release rate of a biocide to prevent the attachment of barnacles and hydrozoans to a well-characterized surface. During the peak summer fouling months at DTRC, Annapolis heavy rains decreased the local salinity to 1-4 parts per thousand for most of the summer. This low salinity effectively eliminated the local larval population. For this reason the entire apparatus was taken to the Chesapeake Biological Laboratory in Solomons, Maryland.

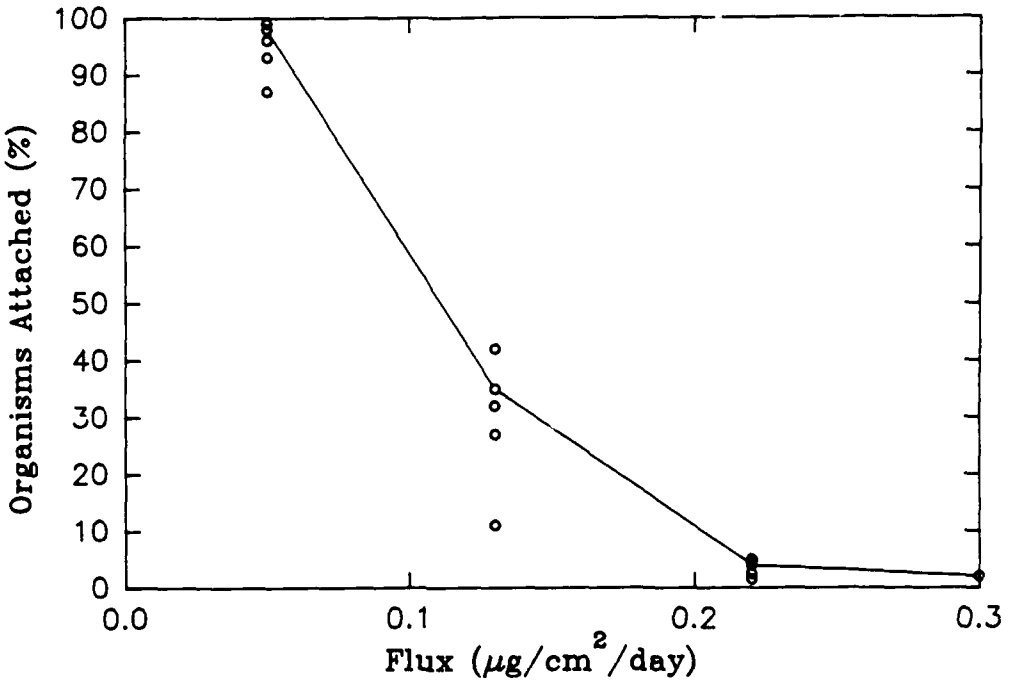

Fig. 1. Percent settlement of barnacles relative to controls vs the flux of tributyltin.

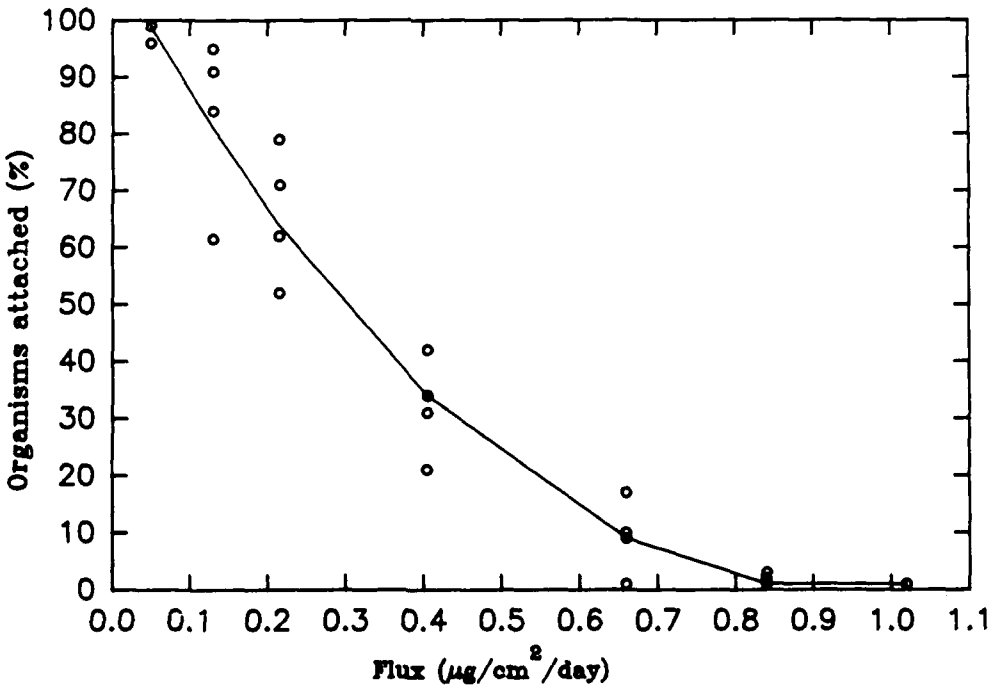

Fig. 2. Percent settlement of hydrozoans relative to controls vs the flux of trubutyltin.

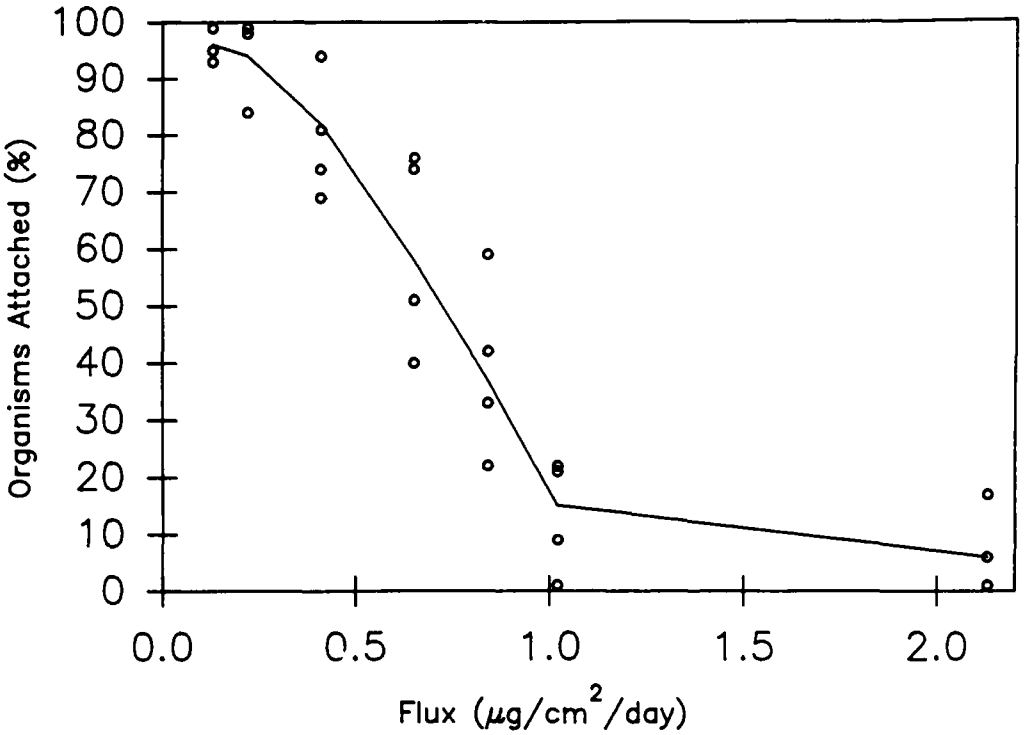

Fig. 3. Percent settlement of barnacles relative to controls vs the flux of dibutyltin.

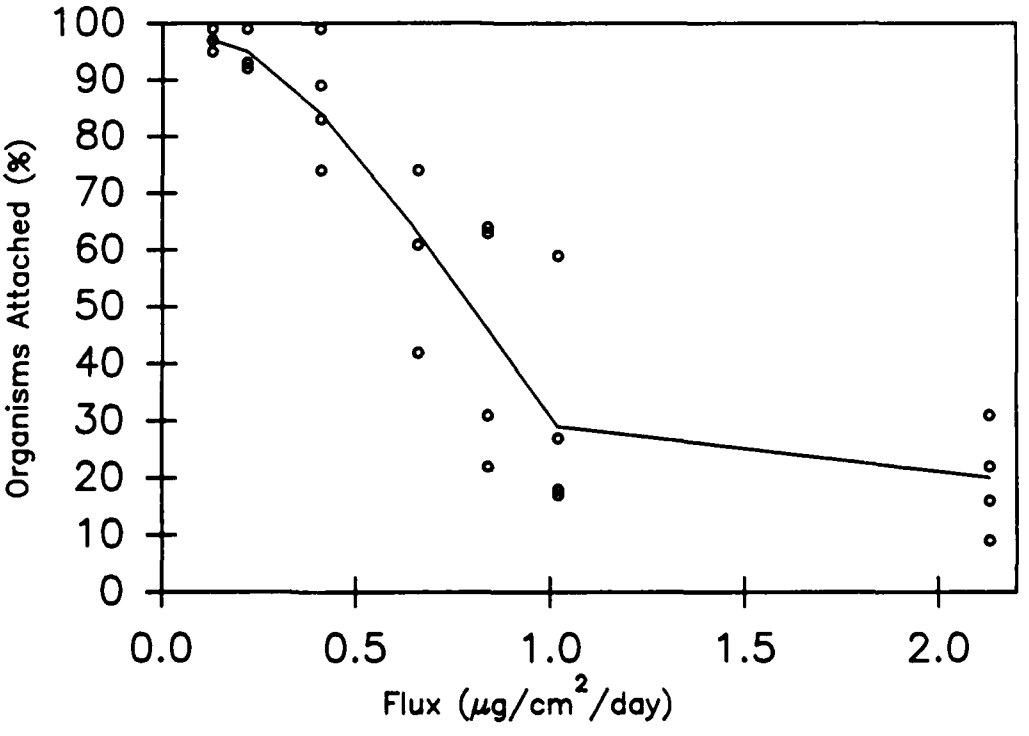

Fig. 4. Percent settlement of hydrozoans relative to controls vs the flux of dibutyltin

Since this site is closer to the mouth of the Chesapeake Bay the salinity values remained higher, with resulting good larval abundance.

In addition to barnacles and hydrozoans, numbers of attaching encrusting bryozoans were also counted. However, the data were not usable for determining the minimum effective release rate because the bryozoans generally attached to one of the organisms already attached to the surface. Very rarely did bryozoans attach directly to the membrane surface. It is not likely that the TBT was preventing them from attaching to the surface since they did not attach to the polycarbonate surfaces of the low flow controls or on the still controls. This could be due to the fact that this species exhibits a preference for settlement on these other organisms or they avoid some characteristic of the polycarbonate surface.

Results indicate that the method is very effective in determining the minimum release value for barnacle and hydroids as well as peritrich slime organisms. In order to determine the fouling free value most of the data must be taken for those flux values at which the fouling approaches the zero level. This work established the minimum effective release rate of 0.22 $\mu g/cm^2/day$ TBT for barnacles and 0.83 $\mu g/cm^2/day$ TBT for hydrozoans. The results from Gates et al. (1) using a variation of this method for a common fouling protozoan, a peritrich, was 2.4 $\mu g/cm^2/day$. This higher value is consistent with observations on ships and with our data because it has been shown that TBT is more effective against macrofoulers than microorganism slime formers such as peritrichs.

It is difficult at this point to obtain relevant release rates of paints of ships for comparison. One reason is that the duty cycle of the ship will affect the amount of TBT being released from the coating. TBT AF paints on a ship underway will have higher TBT release rates those on ships in port. In addition, tidal currents in harbors, and water chemistry parameters such as salinity and temperature will have their effect. Release rate studies for painted panels have shown this to be true. Thus, Takahashi and Ikuta (6) have shown a two fold increase in the release rate when comparing the ASTM method to a method involving passing bubbles past the painted surface. Work at DTRC, Annapolis has shown a 10 fold increase in TBT release rate for some ablative paints (7, 8) when comparing the rotating disk method to a method which involved gentle water flow past the painted panel. These results clearly show that the hydrodynamic regime will determine the TBT release from actual painted surfaces. One virtue of the perfusion method is that it allows predetermination of the precise release rates independent of such parameters. It would be possible, therefore, with this minimum effective release rate method to test the effects of hydrodynamic conditions on settlement at a predetermined known release rate. The dibutyltin flux rates tested were not high enough to determine the minimum effective release rate. This data will be an excellent starting point for continued experimentation with dibutyltin.

FUTURE WORK

The device will be tested at as many remote sites as possible to account for variability in local larval populations. To date the apparatus has been taken to Duke University in Beaufort, NC., and to NOSC at San Diego, CA. Tests are currently underway with TBTCl, and immediate plans include testing combinations of biocides as time permits. More long range plans are being made to contact one or two additional West Coast sites, and a warm-water East Coast site. Tests will focus on TBTCl and combinations of active agents. More complete testing of natural product antifoulants will take place, including continued work at Duke University and work at University of Delaware and DTRC.

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Appendix A

Raw Data for Settlement with Tributyl and Dibutyltin

APPENDIX A

TABLE A1

BARNACLE SETTLEMENT -- TRIBUTYLTIN
NUMBERS OF BARNACLES ON SURFACE

FLUX*	EXP-1	EXP-2	EXP-3	EXP-4
1.02	0	0	0	0
0.84	0	0	0	0
0.66	0	0	1	0
0.41	1	0	0	0
0.22	2	0	0	1
0.13	13	2	16	8
0.05	28	14	49	38
0.00	32	15	51	29
NO FLOW	28	10	64	34
NO FLOW	41	16	48	40

* FLUX= $\mu g/cm^2/day$

TABLE A2

BARNACLE SETTLEMENT -- DIBUTYLTIN
NUMBERS OF BARNACLES ON SURFACE

FLUX*	EXP-1	EXP-2	EXP-3	EXP-4
2.13	1	0	3	4
1.02	6	0	4	13
0.84	30	9	11	20
0.66	28	32	14	32
0.41	53	30	16	58
0.22	70	51	16	75
0.13	83	40	18	68
0.00	71	43	19	62
NO FLOW	64	52	28	80
NO FLOW	68	40	21	40

* FLUX= $\mu g/cm^2/day$

TABLE A3

HYDROZOAN SETTLEMENT -- TRIBUTYLTIN
NUMBERS OF HYDROZOANS ON SURFACE

FLUX*	EXP-1	EXP-2	EXP-3	EXP-4
1.02	0	1	0	0
0.84	0	1	3	1
0.66	11	8	2	6
0.41	34	35	21	13
0.22	68	60	51	29
0.13	92	52	90	35
0.05	122	93	108	36
0.00	110	84	99	37
NO FLOW	98	87	95	38
NO FLOW	112	91	85	30

* FLUX= $\mu g/cm^2/day$

TABLE A4

HYDROZOAN SETTLEMENT -- DIBUTYLTIN
NUMBERS OF HYDROZOANS ON SURFACE

FLUX*	EXP-1	EXP-2	EXP-3	EXP-4
2.13	11	11	32	15
1.02	29	23	28	17
0.84	32	28	65	27
0.66	36	93	62	37
0.41	61	111	75	73
0.22	46	131	94	97
0.13	47	119	99	91
0.00	49	125	102	88
NO FLOW	42	134	92	93
NO FLOW	41	121	95	88

* FLUX= $\mu g/cm^2/day$

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